

ENC-2022-0210

PERFORMANCE PREDICTION OF MICROBIAL FUEL CELLS FOR ACID MINE DRAINAGE TREATMENT AND ENERGY PRODUCTION USING LEAST SQUARES FITTING METHOD

William Francisconi Taufemback

Tatiana Gisset Pineda Vásquez

Priscila Cardoso Calegari

Derce de Oliveira Souza Recouvreux

Regina Vasconcellos Antônio

Elise Sommer Watzko

Universidade Federal de Santa Catarina (UFSC), Campus Araranguá - Rod. Gov. Jorge Lacerda, 3201. Jardim das Avenidas. Araranguá/SC. CEP: 88.906-072.

william.taufemback@posgrad.ufsc.br

latatiss@gmail.com

priscila.calegari@ufsc.br

derce.recouvreux@ufsc.br

regina.antonio@ufsc.br

elise.sommer@ufsc.br

Abstract. *One of the impacts of coal mining is the contamination by Acid Mine Drainage (AMD). Among the alternatives proposed for the AMD treatment, a promising one is through Microbial Fuel Cells (MFCs), whose electrical performance can be characterized by obtaining polarization curves (PCs). Thus, this study proposes an experimental validation of a steady state a model for the prediction of the characteristic equation of the PC of MFCs, applying a least squares fitting to estimate the parameters. The experiments consisted of two double-chamber MFCs operating in fed-batch for 75 days, each separated by different proton exchange membranes (PEM): one used Nafion™ 117 (MFC-NA) and another, bacterial cellulose (MFC-BC). The cathodic chambers were filled with AMD and inoculated with sulfate-reducing bacteria. Experimental PC obtained for MFC-BC showed higher power and current densities than that for MFC-NA. The comparison of the curves obtained by the fitting with experimental data from a study found in the literature, as well as the data from experiments in this paper, demonstrate the potential of the method proposed. In future works, it is expected to test the fitting methodology developed in this paper for different MFC systems, aiming to improve its predictive ability.*

Keywords: *microbial fuel cell, least squares fitting, acid mine drainage, polarization curve, mathematical modeling.*

1. INTRODUCTION

A common environmental problem in coal mining sites, especially at abandoned ones, is the presence of Acid Mine Drainage (AMD), which, if left untreated, can reach surface or groundwater. The AMD results from a series of chemical, electrochemical, and microbiological reactions, which are triggered by exposure of metal sulfides to oxygen and atmospheric water (Alegbe *et al.*, 2019; Skousen *et al.*, 2019).

Generally, the AMD is characterized by a low pH, a high amount of dissolved metals (mainly iron), high values of electrical conductivity and high concentrations of sulfate. Such characteristics are sufficient for the water to be unfit for potable, agricultural, industrial or commercial use (Alegbe *et al.*, 2019; Skousen *et al.*, 2019).

Different technologies have been used for the AMD treatment. An alternative approach is the treatment through Microbial Fuel Cell (MFC), with the possibility of generating electricity in the process. A MFC is a bioelectrochemical system that generates energy from organic compounds with the help of electroactive microorganisms to catalyze oxidation and reduction reactions (Ai *et al.*, 2020; Foudhaili *et al.*, 2019; Hai *et al.*, 2016; Leiva *et al.*, 2016; Peiravi *et al.*, 2017; Peng *et al.*, 2017; Rodrigues and Leão, 2020; Vélez-Pérez *et al.*, 2020).

However, the MFC technology has not been successfully applied on larger scales yet, due to the low performances registered and the high costs of the materials used. Thus, for scale up of MFCs to be possible, in order to make this

technology viable, it is necessary to optimize performance, develop new materials and improve the constructive and design parameters of these devices (Ramya and Kumar, 2022; Vilas Boas *et al.*, 2022).

To optimize the performance of a MFC it is important to characterize its efficiency in terms of electric power generation and an efficient methodology for this is through the construction of polarization curves (PC). These curves relate the voltage and current (or current density) values, and make it possible to identify the main voltage losses (overpotentials) that limit the system (Koók *et al.*, 2021; Serra *et al.*, 2020).

An ideal PC for any fuel cell includes three characteristic regions located at different electrical current ranges where three regions can be identified, each of them associated with an overpotential: the region of charge transfer derived overpotentials, also named activation losses, at low currents; the ohmic overpotentials in the linear region, at intermediate currents; and the mass transport overpotentials region, also named concentration losses, at higher currents (Zhao *et al.*, 2009).

The task of optimizing MFCs is complex, as it requires multidisciplinary concepts from areas such as microbiology, electrochemistry and materials science. Thus, the experimental investigation of the effect of each parameter, either independently or in possible combinations with other parameters, ends up becoming an expensive and time-consuming process (Gadkari *et al.*, 2018; Jadhav *et al.*, 2021; Xia *et al.*, 2018).

An alternative to save time and resources in the process of investigation and optimization of MFCs is through the development of mathematical models, which can be used to simulate different configurations and operational conditions, providing important predictions about the influence on performance that is exerted by different parameters (Deb *et al.*, 2020; Gadkari *et al.*, 2018; Jadhav *et al.*, 2021; Ortiz-Martínez *et al.*, 2015; Recio-Garrido *et al.*, 2016; Xia *et al.*, 2018).

The construction of a mathematical model to represent complex systems can be extremely complicated. One possibility is to represent such systems through empirical correlations, based on experimental data. In this sense, the curve fitting is an efficient methodology to determine the values of the parameters of a model (Charafeddine and Ouardi, 2020).

Therefore, this paper proposes an experimental validation of a developed model and least squares fitting of the performance of a MFC applied to the AMD treatment and electricity generation, enabling the prediction of the characteristic equation of the polarization curve of MFCs in steady state, through the parameters estimation. It is expected that the parameter fitting methodology presented in this paper will help to characterize the efficiency of the MFC system proposed here for electrical energy production.

2. MATERIAL AND METHODS

2.1 MFCs construction and operation

Two double-chamber MFCs were constructed, each from two cylinders (8×33 cm) of plexiglass, joined with a PVC pipe containing a 5 cm diameter proton exchange membrane (PEM). In one MFC (MFC-NA), Nafion™ 117 was used as PEM; for comparison, in another MFC (MFC-BC), bacterial cellulose (BC), produced by *Komagataeibacter hansenii* ATCC 23769, was used as an alternative cheaper PEM. According to Vilela *et al.* (2018), the application of BC as a PEM has potential due its protonic conductivity and mechanical properties.

Anode and cathode electrodes were made of carbon felt (AvCarb™, 2×5 cm), and were connected by a resistor of 1 k Ω by titanium wire. The anodic chambers were filled with 1.9 L of phosphate buffer medium (pH = 7.0), containing 1 g/L sodium acetate and 100 mL of sludge from municipal wastewater treatment plant (Criciúma, Brazil). The cathodic chambers were filled with 1.9 L of AMD (pH approximately 2.8), 1 g/L of sodium lactate, 100 mL of microbiota enriched in sulfate-reducing bacteria (SRB) and 50 g of rice husk, mimicking a selective permeable barrier (SPB). The utilized AMD was from a coal mine located in the city of Treviso (Brazil).

The MFCs were operated in fed-batch for 75 days. Whenever the potential was lower than 100 mV, the entire cathodic solution was replaced, and was added in the anodic chamber glucose (1 g/L) and the phosphate buffer medium, in order to maintain the pH = 7.0. A schematic diagram of the dual-chamber MFC configuration used in this study is shown in Fig. 1.

2.2 Analytical methods

The voltage at external resistor of 1 k Ω was measured and registered using a sensor (WorkTemp™ wt290-ac). A set of seven external resistances (OCV, 1000, 556, 217, 100, 56 and 22 Ω) were used as load to obtain a polarization curve (PC), which was performed on day 75 by the single-cycle method, once the voltage stabilized after the MFC was fed. In the single-cycle method, according to Watson and Logan (2011), each resistance is connected for 20 minutes intervals and the voltage is recorded over a single batch cycle.

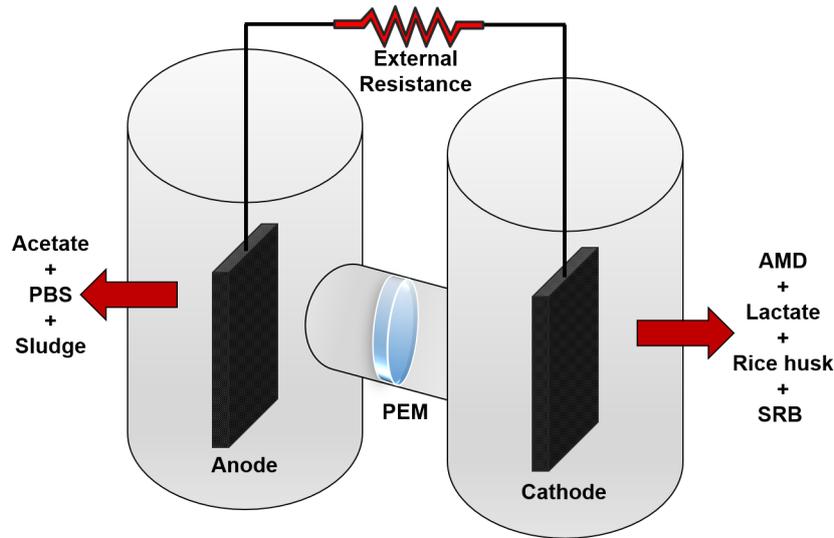


Figure 1. Schematic diagram of the MFC configuration used in this study.

2.3 Steady-state model and least squares fitting method

Serra *et al.* (2020) proposed a method that allows quantifying each of the power losses and identifying their contribution on the overall polarization curve (PC), so that its equation can be estimated. The ohmic overpotential (η_{ohm}), due to their linear behavior, were modeled by Ohm's Law,

$$\eta_{ohm} = a_1 x, \quad (1)$$

where x refers to electrical current, and a_1 to the internal resistance (R_{int}).

Activation losses (η_{act}) were modeled using the Tafel equation,

$$\eta_{act} = a_2 \ln \left(\frac{x}{a_3} + 1 \right), \quad (2)$$

where a_2 is related to the MFC's characteristics, and a_3 represents the relationship between the current density of the MFC and its exchange current density. The exchange current density characterizes the catalytic ability of the electrode (Serra *et al.*, 2020).

Finally, the concentration losses (η_{conc}), was calculate by,

$$\eta_{conc} = a_4 \exp(a_5 x), \quad (3)$$

where a_4 is a constant that depends on the MFC and its operational state, and the parameter a_5 is related to the limiting electrical current, referring to the state where reactant consumption occurs at a rate equal to its maximum supply speed (Serra *et al.*, 2020).

The resulting voltage across the MFC terminals was obtained by subtracting from the theoretical electric potential, simplified by the open circuit voltage, the contributions of each of the potential losses,

$$f(x, \mathbf{a}) = a_0 - a_1 x - a_2 \ln \left(\frac{x}{a_3} + 1 \right) - a_4 \exp(a_5 x), \quad (4)$$

where the term a_0 refers to open circuit voltage (OCV) of MFC (Serra *et al.*, 2020).

The experimental data and steady-state model, showed in Eq. (4) and presented by Serra *et al.* (2020) were employed for fitting the PCs. In order to fit the experimental data to a linear function, it is necessary to obtain the values of parameters a_0 and a_1 in the first two terms of Eq. (4). For fitting the data to a non-linear function, it is necessary to obtain all the values of the parameters \mathbf{a} of Eq. (4). In both adjustments, the parameters were obtained by the least squares fitting method, whose objective is to minimize the residue function given by,

$$r(\mathbf{a}) = \frac{1}{2} \sum_{i=1}^m r_i(\mathbf{a})^2, \quad (5)$$

where the residue is represented by $r_i(\mathbf{a}) = f(x_i, \mathbf{a}) - y_i$. The term \mathbf{a} is a vector with components $a_i (i = 0, 1, \dots, 5)$; x_i and y_i are the experimental data, current (or current density) and voltage, respectively. The fitting of the parameters of the PC curve was made in a computer program written in the *Python* programming language, using the *numpy* and *scipy* libraries.

3. RESULTS AND DISCUSSION

Polarizations curves (PCs) obtained for MFC-BC and MFC-NA are presented in Fig. 2. At the same voltages, the MFC using bacterial cellulose (BC) showed higher power and current densities than that using Nafion™ 117, which was also reported by Vilela *et al.* (2020). During the operation, the maximum power density presented by MFC-BC was also higher (60.84 mW/m^2) than that presented by MFC-NA (37.45 mW/m^2).

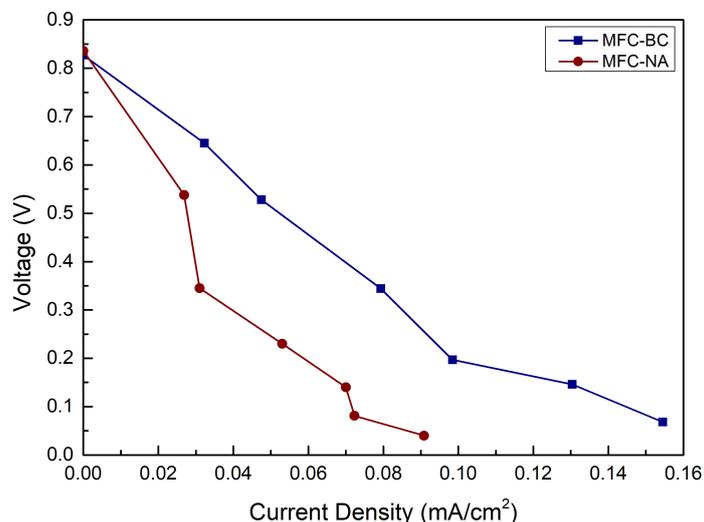


Figure 2. Polarization curves built for MFCs with bacterial cellulose (MFC-BC) and Nafion™ 117 (MFC-NA).

As BC is a material of biological origin, and considering that MFCs are devices where microorganisms are responsible for energy production, a hypothesis for the better results obtained with MFC-BC is that there is more biocompatibility in the medium, providing less impact on the microbiota and, therefore, larger energy production compared to MFC-NA. Furthermore, according to Ko *et al.* (2015), the pristine BC membrane hydrogel properties are believed to promote proton transfer through the hydrogen bond network of water molecules.

Figure 3 presents the experimental data by Serra *et al.* (2020) referring to the day on which a maximum power density was achieved, and the PC obtained by the non-linear fit performed in our fitting. The non-linear fit presents a good correlation with the behavior of the polarization experimental data.

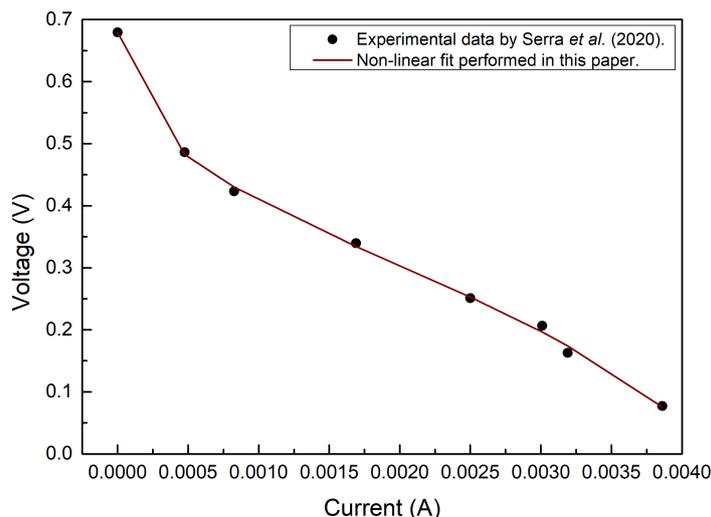


Figure 3. Comparison between the experimental polarization data reported by Serra *et al.* (2020) and those obtained by the non-linear fit in this study.

A comparison between the parameters estimated by Serra *et al.* (2020) and those estimated in this work by the non-linear fit can be seen in the Tab. 1. The values of the parameters estimated were very close to the values reported by the author, with sum of the squares of the differences between the estimated values and the observed data (i.e. the residual value), calculated by Eq. (5), $r(\mathbf{a}) = 1.645 \times 10^{-4}$.

Table 1. Parameters estimated by Serra *et al.* (2020) and those estimated in this study.

Parameter	Serra <i>et al.</i> (2020)	Present work
a_0 (OCV)	0.6795 V (fixed)	0.6795 V (fixed)
a_1 (R_{int})	50.51 Ω	50.56 Ω
a_2	0.06365	0.06394
a_3	0.00003628	0.00003672
a_4	0.002671	0.002628
a_5	967.4	968.8

Figure 4 presents the PC from non-linear fit for the experimental polarization data of MFC-BC. The non-linear fit from PC to MFC with bacterial cellulose show good correspondence in graphics. Figure 5 shows the PC from non-linear fit for the experimental polarization data of MFC-NA. The non-linear fit from PC to MFC with Nafion™ 117 showed a linear profile, although it follows the PC trend. The residual values for MFC-BC and MFC-NA are, respectively, $r(\mathbf{a}) = 1.707 \times 10^{-3}$ and $r(\mathbf{a}) = 1.868 \times 10^{-2}$.

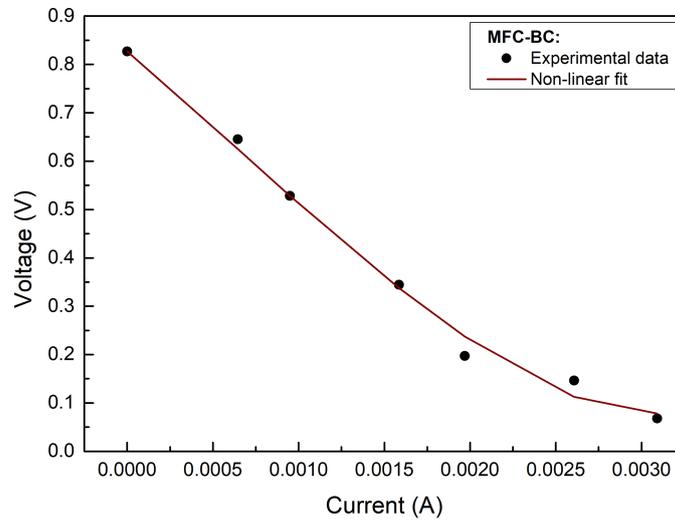


Figure 4. Comparison between the experimental polarization data and those obtained by the non-linear fit for MFC-BC.

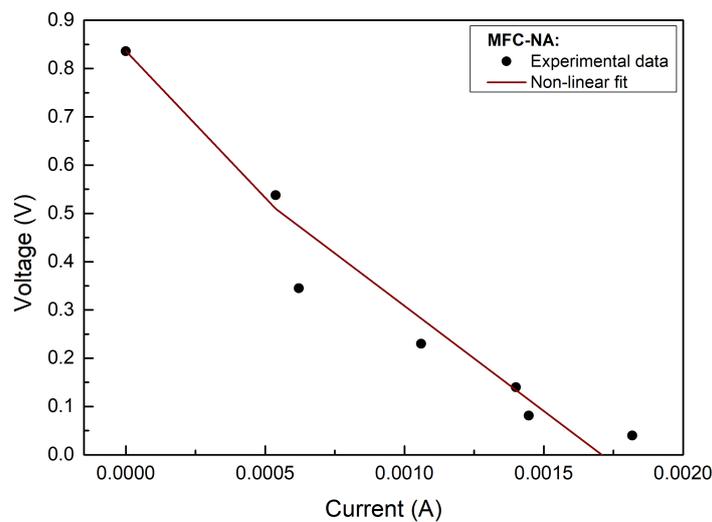


Figure 5. Comparison between the experimental polarization data and those obtained by the non-linear fit for MFC-NA.

The estimated parameters for the experimental polarization data of MFC-BC and MFC-NA are showed in Tab. 2. The internal resistance obtained for the MFC using Nafion™ 117 as a PEM is almost three times higher (442.1 Ω) than that obtained for the MFC using BC membrane as a PEM (151.7 Ω). The high internal resistance presented by the MFC-NA can be observed by the predominance of the linearity region in its polarization curve (Fig. 5).

Table 2. Parameters estimated by non-linear regression for MFC-BC and MFC-NA.

Parameter	MFC-BC	MFC-NA
a_0 (OCV)	0.827 V (fixed)	0.836 V (fixed)
a_1 (R_{int})	151.7 Ω	442.1 Ω
a_2	-101.3	-503.1
a_3	-0.5041	77.19
a_4	-0.01327	0.09195
a_5	1052.5	0.06209

Additionally, considering the linear characteristic of the experimental polarization curve of MFC-NA (Fig. 5), a linear fit was performed, also shown in Fig. 6, which resulted in the following coefficients and residual: $a_0 = 0.74405$ V; $a_1 = 435.62$ Ω ; and $r(\mathbf{a}) = 1.868 \times 10^{-2}$.

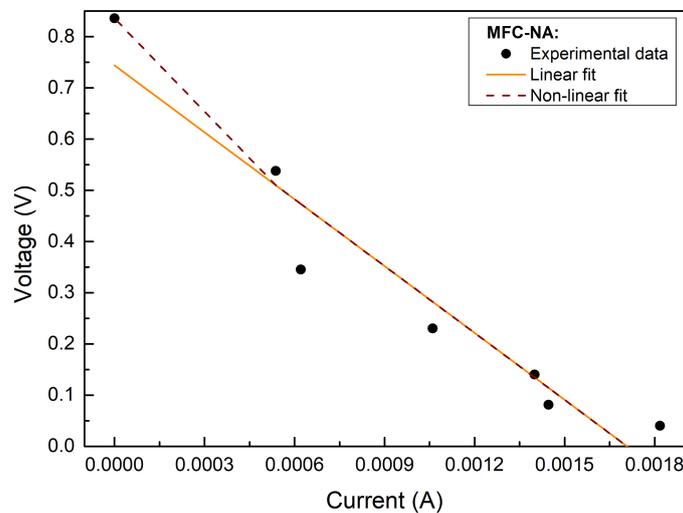


Figure 6. Comparison between the experimental polarization data and those obtained by the linear and non-linear fits for MFC-NA.

Therefore, in future studies, it is intended to experimentally verify the ohmic resistance value through the electrochemical impedance spectroscopy (EIS) analysis, as done by Hidalgo *et al.* (2015), to analyze internal resistance values in a MFC system.

4. CONCLUSIONS

The feasibility of the MFC system proposed here in electricity generation from AMD was demonstrated. The MFC with BC as a PEM showed higher power and current densities than that using Nafion™ 117, indicating that BC membrane can be a more economical substitute for energy production in these devices.

This study also proposed a computational method to estimate parameters and predict the PC shape of MFCs, based on a mathematical model presented in a previous study (Serra *et al.*, 2020). The comparison of the curves obtained by the fitting with experimental data from the aforementioned previous study, as well as the data from experiments in this work, demonstrate the potential of the method proposed here. In future works, it is expected to test this method for PCs from MFCs with different architectures and conditions, aiming to improve its predictive ability.

5. ACKNOWLEDGEMENTS

This study was supported in part by the Fundação de Amparo e Inovação à Pesquisa do Estado de Santa Catarina – Brazil (FAPESC) – N° 2021TR000582 and N° UNI2020121000332; and by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – N° 88887.659004/2021-00. All experiments were conducted in the Laboratório de Processos Biotecnológicos Inovadores (PROBIOTEC) of Universidade Federal de Santa Catarina (UFSC). The authors wish to acknowledge Prof. Juarez Bento da Silva and the staff of Laboratório de Experimentação Remota (RExLab) of UFSC for their help in the design and implementation of the data acquisition system.

6. REFERENCES

- Ai, C., Yan, Z., Hou, S., Zheng, X., Zeng, Z., Amanze, C., Dai, Z., Chai, L., Qiu, G. and Zeng, W., 2020. "Effective treatment of acid mine drainage with microbial fuel cells: An emphasis on typical energy substrates". *Minerals*, Vol. 10, No. 5, p. 443.
- Alegbe, M., Ayanda, O., Ndungu, P., Nechaev, A., Fatoba, O. and Petrik, L., 2019. "Physicochemical characteristics of acid mine drainage, simultaneous remediation and use as feedstock for value added products". *Journal of Environmental Chemical Engineering*, Vol. 7, No. 3, p. 103097.
- Charafeddine, K. and Ouardi, F., 2020. "Novel methodology to determine leakage power in standard cell library design". *Heliyon*, Vol. 6, No. 6, p. e04168.
- Deb, D., Patel, R. and Balas, V.E., 2020. "A review of control-oriented bioelectrochemical mathematical models of microbial fuel cells". *Processes*, Vol. 8, No. 5, p. 583.
- Foudhaili, T., Rakotonimaro, T.V., Neculita, C.M., Coudert, L. and Lefebvre, O., 2019. "Comparative efficiency of microbial fuel cells and electrocoagulation for the treatment of iron-rich acid mine drainage". *Journal of Environmental Chemical Engineering*, Vol. 7, No. 3, p. 103149.
- Gadkari, S., Gu, S. and Sadhukhan, J., 2018. "Towards automated design of bioelectrochemical systems: A comprehensive review of mathematical models". *Chemical Engineering Journal*, Vol. 343, pp. 303–316.
- Hai, T., Wen-Cheng, P., Chang-Feng, C., Jian-Ping, X. and Wen-Jun, H., 2016. "Remediation of acid mine drainage based on a novel coupled membrane-free microbial fuel cell with permeable reactive barrier system." *Polish Journal of Environmental Studies*, Vol. 25, No. 1.
- Hidalgo, D., Sacco, A., Hernández, S. and Tommasi, T., 2015. "Electrochemical and impedance characterization of microbial fuel cells based on 2d and 3d anodic electrodes working with seawater microorganisms under continuous operation". *Bioresource Technology*, Vol. 195, pp. 139–146.
- Jadhav, D.A., Carmona-Martínez, A.A., Chendake, A.D., Pandit, S. and Pant, D., 2021. "Modeling and optimization strategies towards performance enhancement of microbial fuel cells". *Bioresource Technology*, Vol. 320, p. 124256.
- Ko, Y.H., Oh, H.J. and Lee, H.J., 2015. "Use of bacterial cellulose from *gluconacetobacter hansenii* nok21 as a proton-permeable membrane in microbial fuel cells". *Journal of Microbial Biochemical Technology*, Vol. 7, No. 3, pp. 145–151.
- Koók, L., Nemestóthy, N., Bélafi-Bakó, K. and Bakonyi, P., 2021. "The influential role of external electrical load in microbial fuel cells and related improvement strategies: a review". *Bioelectrochemistry*, Vol. 140, p. 107749.
- Leiva, E., Leiva-Aravena, E. and Vargas, I., 2016. "Acid water neutralization using microbial fuel cells: An alternative for acid mine drainage treatment". *Water*, Vol. 8, No. 11, p. 536.
- Ortiz-Martínez, V., Salar-García, M., De Los Ríos, A., Hernández-Fernández, F., Egea, J. and Lozano, L., 2015. "Developments in microbial fuel cell modeling". *Chemical Engineering Journal*, Vol. 271, pp. 50–60.
- Peiravi, M., Mote, S.R., Mohanty, M.K. and Liu, J., 2017. "Bioelectrochemical treatment of acid mine drainage (amd) from an abandoned coal mine under aerobic condition". *Journal of hazardous materials*, Vol. 333, pp. 329–338.
- Peng, X., Tang, T., Zhu, X., Jia, G., Ding, Y., Chen, Y., Yang, Y. and Tang, W., 2017. "Remediation of acid mine drainage using microbial fuel cell based on sludge anaerobic fermentation". *Environmental Technology*, Vol. 38, No. 19, pp. 2400–2409.
- Ramya, M. and Kumar, P.S., 2022. "A review on recent advancements in bioenergy production using microbial fuel cells". *Chemosphere*, Vol. 288, p. 132512.
- Recio-Garrido, D., Perrier, M. and Tartakovsky, B., 2016. "Modeling, optimization and control of bioelectrochemical systems". *Chemical Engineering Journal*, Vol. 289, pp. 180–190.
- Rodrigues, I.C.B. and Leão, V.A., 2020. "Producing electrical energy in microbial fuel cells based on sulphate reduction: a review". *Environmental Science and Pollution Research*, Vol. 27, No. 29, pp. 36075–36084.
- Serra, P., Espírito-Santo, A. and Magrinho, M., 2020. "A steady-state electrical model of a microbial fuel cell through multiple-cycle polarization curves". *Renewable and Sustainable Energy Reviews*, Vol. 117, p. 109439.
- Skousen, J.G., Ziemkiewicz, P.F. and McDonald, L.M., 2019. "Acid mine drainage formation, control and treatment: Approaches and strategies". *The Extractive Industries and Society*, Vol. 6, No. 1, pp. 241–249.
- Vélez-Pérez, L., Ramirez-Nava, J., Hernández-Flores, G., Talavera-Mendoza, O., Escamilla-Alvarado, C., Poggi-Valardo, H., Solorza-Feria, O. and López-Díaz, J., 2020. "Industrial acid mine drainage and municipal wastewater co-treatment by dual-chamber microbial fuel cells". *International Journal of Hydrogen Energy*, Vol. 45, No. 26, pp. 13757–13766.
- Vilas Boas, J., Oliveira, V.B., Simões, M. and Pinto, A.M., 2022. "Review on microbial fuel cells applications, developments and costs". *Journal of Environmental Management*, Vol. 307, p. 114525.
- Vilela, C., Cordeiro, D.M., Boas, J.V., Barbosa, P., Nolasco, M., Vaz, P.D., Rudić, S., Ribeiro-Claro, P., Silvestre, A.J., Oliveira, V.B. *et al.*, 2020. "Poly (4-styrene sulfonic acid)/bacterial cellulose membranes: Electrochemical performance in a single-chamber microbial fuel cell". *Bioresource Technology Reports*, Vol. 9, p. 100376.
- Vilela, C., Martins, A.P., Sousa, N., Silvestre, A.J., Figueiredo, F.M. and Freire, C.S., 2018. "Poly (bis [2-

(methacryloyloxy) ethyl] phosphate)/bacterial cellulose nanocomposites: Preparation, characterization and application as polymer electrolyte membranes”. *Applied Sciences*, Vol. 8, No. 7, p. 1145.

Watson, V.J. and Logan, B.E., 2011. “Analysis of polarization methods for elimination of power overshoot in microbial fuel cells”. *Electrochemistry Communications*, Vol. 13, No. 1, pp. 54–56.

Xia, C., Zhang, D., Pedrycz, W., Zhu, Y. and Guo, Y., 2018. “Models for microbial fuel cells: a critical review”. *Journal of Power Sources*, Vol. 373, pp. 119–131.

Zhao, F., Slade, R.C. and Varcoe, J.R., 2009. “Techniques for the study and development of microbial fuel cells: an electrochemical perspective”. *Chemical Society Reviews*, Vol. 38, No. 7, pp. 1926–1939.

7. RESPONSIBILITY NOTICE

The authors are solely responsible for the printed material included in this paper.